

(19)



Europäisches Patentamt
European Patent Office
Office européen des brevets



(11)

EP 1 162 675 A2

(12)

EUROPEAN PATENT APPLICATION

(43) Date of publication:
12.12.2001 Bulletin 2001/50

(51) Int Cl.7: **H01M 4/02, H01M 10/40**

(21) Application number: **01305020.8**

(22) Date of filing: **08.06.2001**

(84) Designated Contracting States:
**AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU
MC NL PT SE TR**
Designated Extension States:
AL LT LV MK RO SI

(30) Priority: **08.06.2000 JP 2000172073**

(71) Applicant: **Sumitomo Electric Industries, Ltd.
Osaka-shi, Osaka 541-0041 (JP)**

(72) Inventors:
• **Kugai, Hirokazu**
1-1 Koyakita 1-chome, Itami-shi, Hyogo (JP)

• **Ota, Nobuhiro**
1-1 Koyakita 1-chome, Itami-shi, Hyogo (JP)
• **Yamanaka, Shosaku**
1-1 Koyakita 1-chome, Itami-shi, Hyogo (JP)

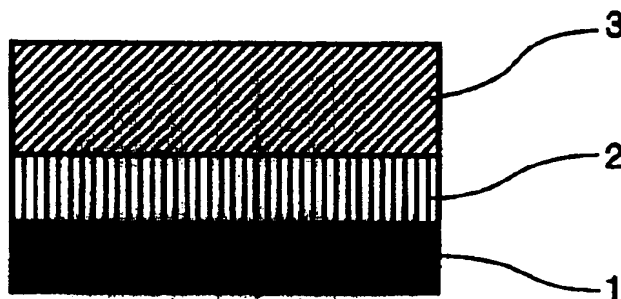
(74) Representative:
Cross, Rupert Edward Blount et al
BOULT WADE TENNANT,
Verulam Gardens
70 Gray's Inn Road
London WC1X 8BT (GB)

(54) **Negative electrode of lithium secondary battery**

(57) A lithium-secondary-battery negative electrode having a protective layer to prevent the surface deterioration of the inorganic solid electrolytic layer. The negative electrode comprises metallic lithium or a lithium-

containing metal, a first inorganic solid electrolytic layer (thickness: *a*) formed on the metal, and a second inorganic solid electrolytic layer (thickness: *b*) formed on the first inorganic solid electrolytic layer. The thickness ratio *b/a* is specified to be more than 0.5.

FIG. 1



EP 1 162 675 A2

Description

[0001] The present invention relates to a material for the negative electrode of a lithium secondary battery.

[0002] Lithium secondary batteries having organic electrolysis solutions have been widely used. Their advantage is the high energy output per unit volume or unit weight in comparison with other batteries. In exploiting this advantage, researchers and engineers have been advancing the development and practical applications of the batteries as power sources for mobile communication devices, notebook-type personal computers, and electric cars.

[0003] In order to improve the performance of a lithium secondary battery, attempts have been made to use metallic lithium as the negative electrode. However, the repetition of charge and discharge causes dendritic metallic lithium to grow on the surface of the negative electrode. This may lead to an internal short circuit between the negative and positive electrodes, ultimately triggering explosion. To avoid this hazardous situation, engineers have been studying the formation of an inorganic solid electrolytic layer as the electrolyte on the metallic lithium. They have also been studying the formation of a protective layer to prevent the surface deterioration of the inorganic solid electrolytic layer.

[0004] However, it remains to be found how the thickness of the inorganic solid electrolytic layer and the protective layer is to be selected in order to obtain a lithium secondary battery having high charge-discharge efficiency and an excellent charge-discharge-cycle performance.

[0005] If the inorganic solid electrolytic layer is excessively thick, the prolonged film-formation time increases the production cost, and bending or other external force exerted during the battery-manufacturing process tends to generate large cracks in the layer.

[0006] An object of the present invention is to offer negative electrode that provides excellent performance to a lithium secondary battery.

[0007] The present invention offers a lithium-secondary-battery negative electrode that comprises metallic lithium or a lithium-containing metal, a first inorganic solid electrolytic layer formed on the metal, and a second inorganic solid electrolytic layer formed as a protective layer on the first inorganic solid electrolytic layer. In the foregoing negative electrode, when the ratio of the thickness b of the second inorganic solid electrolytic layer to the thickness a of the first inorganic solid electrolytic layer b/a is more than 0.5, a lithium secondary battery that has an excellent charge-discharge-cycle performance can be obtained. It is more desirable that the ratio b/a be 1 or more.

[0008] However, if the second inorganic solid electrolytic layer is excessively thick, although the effect of coating is enhanced, the ionic conductivity decreases and the amount of the second inorganic solid electrolytic layer that dissolves in the electrolyte increases, thereby degrading the performance of the battery. Therefore, it is desirable that the foregoing ratio b/a be less than 2.

[0009] It is desirable that the thickness a of the first inorganic solid electrolytic layer be less than $1\text{ }\mu\text{m}$. The thickness less than $1\text{ }\mu\text{m}$ can reduce the production cost and suppress the generation of large cracks when bending or other external force is exerted on the layer during the battery-manufacturing process.

[0010] The first inorganic solid electrolytic layer may comprise a sulfide-containing lithium-ion-conductive compound, desirably a sulfide-containing lithium-ion-conductive compound that contains at least one member selected from the group consisting of Li_3PO_4 , Li_4SiO_4 , and Li_2SO_4 .

[0011] It is desirable that the second inorganic solid electrolytic layer comprise a constituent contained in the first inorganic solid electrolytic layer except sulfide. This condition enables a satisfactory second inorganic solid electrolytic layer to grow on the first inorganic solid electrolytic layer. The second inorganic solid electrolytic layer may comprise a lithium compound containing at least one member selected from the group consisting of Li_3PO_4 , Li_4SiO_4 , and Li_2SO_4 .

[0012] The first and second inorganic solid electrolytic layers may be amorphous.

[0013] The present invention enables the production of a highly stable lithium secondary battery having high energy density and an excellent charge-discharge-cycle performance.

[0014] The following drawing is provided by way of example.

[0015] Figure 1 is a diagram showing the constitution of the lithium-secondary-battery negative electrode of the present invention.

[0016] Concrete embodiments of the present invention are explained in the following examples. The present invention, however, is not limited by these examples.

[0017] As shown in Fig. 1, the lithium-secondary-battery negative electrode of the present invention comprises metallic lithium or a lithium-containing metal 1, a first inorganic solid electrolytic layer 2, and a second inorganic solid electrolytic layer 3.

EXAMPLE 1

[0018] A sheet of copper foil, $100\text{ }\mu\text{m}$ in thickness and $100 \times 50\text{ mm}$ in size, to be used as a collector was laminated with a sheet of metallic-lithium foil having a thickness of $50\text{ }\mu\text{m}$ and the same size as the copper foil. A first inorganic solid electrolytic layer was formed on the metallic lithium by the sputtering method using an $\text{Li}_2\text{S-SiS}_2\text{-Li}_3\text{PO}_4$ target

in an argon-gas atmosphere at room temperature. A second inorganic solid electrolytic layer was formed as a protective layer on the first inorganic solid electrolytic layer by the sputtering method using an Li_3PO_4 target in an argon-gas atmosphere at room temperature. The thickness of the layers was varied. Tables 1 and 2 show the thickness a of the first inorganic solid electrolytic layer, the thickness b of the second inorganic solid electrolytic layer, and the ratio b/a of the produced samples.

Table 1

Sample No.	Thickness a (μm)	Thickness b (μm)	b/a	Battery performance
1-1	0.8	0.45	0.56	Δ
1-2	0.8	0.6	0.75	\circ
1-3	0.8	0.8	1	\odot
1-4	0.8	1.4	1.75	\odot
1-5	0.8	1.6	2	\circ
1-6	0.8	2.4	3	\circ
Note: \odot : stable after 500 cycles or more \circ : stable after 300 cycles or more and less than 500 cycles Δ : stable after 100 cycles or more and less than 300 cycles				

Table 2

Sample No.	Thickness a (μm)	Thickness b (μm)	b/a	Battery performance
2-1	3	4.5	1.5	\circ
2-2	1	1.5	1.5	\circ
2-3	0.8	1.2	1.5	\odot
2-4	0.1	0.15	1.5	\odot
2-5	1	3	3	Δ
2-6	0.8	2.4	3	\circ
2-7	0.1	0.3	3	\circ
Note: \odot : stable after 500 cycles or more \circ : stable after 300 cycles or more and less than 500 cycles Δ : stable after 100 cycles or more and less than 300 cycles				

[0019] The structure of the negative electrode was the same as that shown in Fig. 1; i.e., the negative electrode comprised metallic lithium, a first inorganic solid electrolytic layer, and a second inorganic solid electrolytic layer. X-ray diffraction results showed that these inorganic solid electrolytic layers were amorphous.

[0020] An electrolyte, LiPF_6 , was dissolved in a mixed liquid of ethylene carbonate (EC) and propylene carbonate (PC). The mixed liquid was heated to dissolve polyacrylonitrile (PAN). Thus, the mixed liquid contained a high concentration of PAN. The mixed liquid was cooled to obtain a gelatinous electrolyte comprising LiPF_6 , EC, PC, and PAN. A powder of LiCoO_2 to be used as an active material and a carbon powder that gives electronic conductivity were mixed into the gelatinous electrolyte. The gelatinous electrolyte was applied onto a sheet of aluminum foil (a positive-electrode-side collector), 20 μm in thickness, to obtain a positive electrode. The layer of the gelatinous electrolyte had a thickness of 300 μm . The metallic lithium on which inorganic solid electrolytic layers were formed was coupled with the foregoing positive electrode to produce a battery.

[0021] The charge and discharge performance of the produced batteries was evaluated. Each battery showed the following results: With a charged voltage of 4.2 V, when the battery was discharged at a rate of 100 mA, it showed a current capacity of 0.5 Ah (ampere hour) before the terminal voltage decreased to 3.5 V. The energy density was 490 Wh/l (watt hour/liter).

[0022] The charge and discharge cycle was repeated 500 times or more under the same condition as described above. The results are shown in Tables 1 and 2. In the column "battery performance" in these tables, the sign " \odot " signifies that the battery was stable after 500 cycles or more; " \circ ", stable after 300 cycles or more and less than 500 cycles; and " Δ ", stable after 100 cycles or more and less than 300 cycles.

[0023] The performance-evaluation results in Table 1 demonstrate that it is necessary that the ratio of the thickness b of the second inorganic solid electrolytic layer to the thickness a of the first inorganic solid electrolytic layer b/a be

more than 0.5. The results also demonstrate that it is desirable that the ratio b/a be 1 or more, and less than 2.

[0024] The performance-evaluation results in Table 2 demonstrate that it is desirable that the thickness a of the first inorganic solid electrolytic layer be less than 1 μm .

EXAMPLE 2

[0025] In the structure used in Example 1, the first inorganic solid electrolytic layer was changed to an $\text{Li}_2\text{S-SiS}_2\text{-Li}_4\text{SiO}_4$ composition and the second inorganic solid electrolytic layer was changed to Li_4SiO_4 . With other conditions unchanged, experiments similar to those in Example 1 were carried out. The results obtained were the same as those shown in Tables 1 and 2.

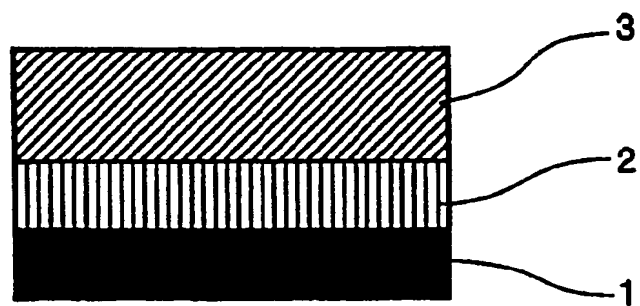
EXAMPLE 3

[0026] In the structure used in Example 1, the first inorganic solid electrolytic layer was changed to an $\text{Li}_2\text{S-SiS}_2\text{-Li}_2\text{SO}_4$ composition and the second inorganic solid electrolytic layer was changed to Li_2SO_4 . With other conditions unchanged, experiments similar to those in Example 1 were carried out. The results obtained were the same as those shown in Tables 1 and 2.

Claims

1. A lithium-secondary-battery negative electrode comprising metallic lithium or a lithium-containing metal, a first inorganic solid electrolytic layer formed on the metal, and a second inorganic solid electrolytic layer formed on the first inorganic solid electrolytic layer, in which the ratio of the thickness b of the second inorganic solid electrolytic layer to the thickness a of the first inorganic solid electrolytic layer b/a is more than 0.5.
2. The lithium-secondary-battery negative electrode as defined in claim 1, wherein the ratio b/a is 1 or more.
3. The lithium-secondary-battery negative electrode as defined in claim 2, wherein the ratio b/a is less than 2.
4. A lithium-secondary-battery negative electrode as defined in any of claims 1 to 3, wherein the thickness a is less than 1 μm .
5. A lithium-secondary-battery negative electrode as defined in any of claims 1 to 4, wherein the first inorganic solid electrolytic layer is a lithium-ion-conductive compound containing sulfide.
6. The lithium-secondary-battery negative electrode as defined in claim 5, wherein the first inorganic solid electrolytic layer contains at least one member selected from the group consisting of Li_3PO_4 , Li_4SiO_4 , and Li_2SO_4 .
7. A lithium-secondary-battery negative electrode as defined in any of claims 1 to 6, wherein the second inorganic solid electrolytic layer is a lithium-ion-conductive compound containing no sulfide.
8. The lithium-secondary-battery negative electrode as defined in claim 7, wherein the second inorganic solid electrolytic layer is a lithium compound containing at least one member selected from the group consisting of Li_3PO_4 , Li_4SiO_4 , and Li_2SO_4 .
9. A lithium-secondary-battery negative electrode as defined in any of claims 1 to 8, wherein the first and second inorganic solid electrolytic layers are amorphous.
10. A lithium-secondary battery comprising a lithium-secondary battery negative electrode as defined in any one of claims 1 to 9.

FIG. 1



THIS PAGE BLANK (USPTO)

(19)



Europäisches Patentamt
European Patent Office
Office européen des brevets



(11)

EP 1 162 675 A3

(12)

EUROPEAN PATENT APPLICATION

(88) Date of publication A3:
08.09.2004 Bulletin 2004/37

(51) Int Cl.7: **H01M 10/36, H01M 4/02,
H01M 10/40**

(43) Date of publication A2:
12.12.2001 Bulletin 2001/50

(21) Application number: **01305020.8**

(22) Date of filing: **08.06.2001**

(84) Designated Contracting States:
**AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU
MC NL PT SE TR**
Designated Extension States:
AL LT LV MK RO SI

- **Ota, Nobuhiro**
1-1 Koyakita 1-chome, Itami-shi, Hyogo (JP)
- **Yamanaka, Shosaku**
1-1 Koyakita 1-chome, Itami-shi, Hyogo (JP)

(30) Priority: **08.06.2000 JP 2000172073**

(71) Applicant: **Sumitomo Electric Industries, Ltd.**
Osaka-shi, Osaka 541-0041 (JP)

(74) Representative:
Cross, Rupert Edward Blount et al
BOULT WADE TENNANT,
Verulam Gardens
70 Gray's Inn Road
London WC1X 8BT (GB)

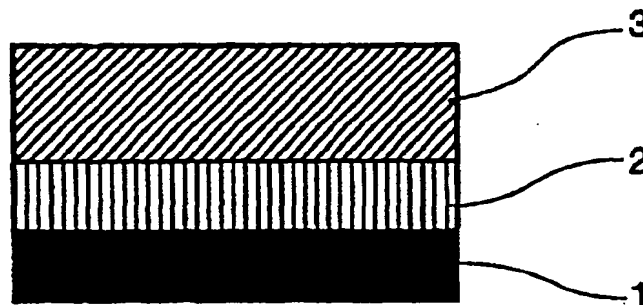
(72) Inventors:
• **Kugai, Hirokazu**
1-1 Koyakita 1-chome, Itami-shi, Hyogo (JP)

(54) Negative electrode of lithium secondary battery

(57) A lithium-secondary-battery negative electrode having a protective layer to prevent the surface deterioration of the inorganic solid electrolytic layer. The negative electrode comprises metallic lithium or a lithium-

containing metal, a first inorganic solid electrolytic layer (thickness: *a*) formed on the metal, and a second inorganic solid electrolytic layer (thickness: *b*) formed on the first inorganic solid electrolytic layer. The thickness ratio *b/a* is specified to be more than 0.5.

FIG. 1



EP 1 162 675 A3



European Patent
Office

PARTIAL EUROPEAN SEARCH REPORT

Application Number

which under Rule 45 of the European Patent Convention shall be considered, for the purposes of subsequent proceedings, as the European search report

EP 01 30 5020

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
P, X, L	EP 1 052 718 A (SUMITOMO ELECTRIC INDUSTRIES) 15 November 2000 (2000-11-15) "L" so quoted as doubt on priority * page 5, line 1 - page 6, line 14 * * page 7, line 46 - page 7, column 47 * EXAMPLES 2-1 TO 2-3 AND 4-16 TO 4-20 * claims 11,12 *	1-10	H01M10/36 H01M4/02 H01M10/40
X	US 5 314 765 A (BATES JOHN B) 24 May 1994 (1994-05-24) * column 2, line 33 - column 3, line 21; claims 3-10 *	1-4,7-10	
P, X, L	PATENT ABSTRACTS OF JAPAN vol. 2000, no. 15, 6 April 2001 (2001-04-06) -& JP 2000 340257 A (SUMITOMO ELECTRIC IND LTD), 8 December 2000 (2000-12-08) "L" so quoted as doubt on priority * abstract *	1-10	
			TECHNICAL FIELDS SEARCHED (Int.Cl.7)
			H01M
INCOMPLETE SEARCH <p>The Search Division considers that the present application, or one or more of its claims, does/do not comply with the EPC to such an extent that a meaningful search into the state of the art cannot be carried out, or can only be carried out partially, for these claims.</p> <p>Claims searched completely :</p> <p>Claims searched incompletely :</p> <p>Claims not searched :</p> <p>Reason for the limitation of the search:</p> <p>see sheet C</p>			
Place of search		Date of completion of the search	Examiner
The Hague		20 July 2004	Crottaz, O
CATEGORY OF CITED DOCUMENTS <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document</p>			

EPO FORM 1503 (03/02) (P/4C/D7)

European Patent
OfficeINCOMPLETE SEARCH
SHEET CApplication Number
EP 01 30 5020

Claim(s) searched incompletely:
1-10

Claim(s) not searched:
-

Reason for the limitation of the search:

Present claims 1-4 relate to a product defined by reference to the ratio of the thicknesses of the two inorganic solid electrolytic layers. The claims cover all products/apparatus having this characteristic or property, whereas the application provides support within the meaning of Article 84 EPC and/or disclosure within the meaning of Article 83 EPC for only a very limited number of such products. In the present case, the claims so lack support, and the application so lacks disclosure, that a meaningful search over the whole of the claimed scope is impossible. Further, present claims 5-10 relate to an extremely large number of possible compounds. Support within the meaning of Article 84 EPC and/or disclosure within the meaning of Article 83 EPC is to be found, however, for only a very small proportion of the compounds claimed. In the present case, the claims so lack support, and the application so lacks disclosure, that a meaningful search over the whole of the claimed scope is impossible. Consequently, the search has been carried out for those parts of the claims which appear to be supported and disclosed in the application, namely where the lithium-ion conductive compound containing sulfide in the first inorganic electrolytic layer is Li_2S and SiS_2 and where the compound containing no sulfide in the second inorganic electrolytic layer is a member selected from Li_3PO_4 , Li_4SiO_4 and Li_2SO_4 .



European Patent
Office

PARTIAL EUROPEAN SEARCH REPORT

Application Number
EP 01 30 5020

DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	
X	PATENT ABSTRACTS OF JAPAN vol. 1995, no. 02, 31 March 1995 (1995-03-31) - & JP 06 310125 A (MITSUBISHI CABLE IND LTD), 4 November 1994 (1994-11-04) * abstract *	1-4, 7, 9, 10	
A	EP 0 469 574 A (MATSUSHITA ELECTRIC IND CO LTD) 5 February 1992 (1992-02-05) * column 2, line 31 - column 3, line 9; examples 2-7 *	5-8	
A	IWAMOTO K ET AL: "RECHARGEABLE SOLID STATE BATTERY WITH LITHIUM CONDUCTIVE GLASS, Li3PO4-Li2S-SiS2" SOLID STATE IONICS, NORTH HOLLAND PUB. COMPANY, AMSTERDAM, NL, vol. 70/71, no. PART 1, 1994, pages 658-661, XP001196944 ISSN: 0167-2738 * paragraph '0002! - paragraph '0003! *	1-10	TECHNICAL FIELDS SEARCHED (Int.Cl.7)
A	US 5 085 953 A (AKRIDGE JAMES R ET AL) 4 February 1992 (1992-02-04) * column 2, line 1 - column 3, line 29; example 12 *	1-4, 7, 8	
A	IWAMOTO K ET AL: "Application of Li3PO4-Li2S-SiS2 glass to the solid state secondary batteries" SOLID STATE IONICS, NORTH HOLLAND PUB. COMPANY, AMSTERDAM, NL, vol. 79, 1 July 1995 (1995-07-01), pages 288-291, XP004050357 ISSN: 0167-2738 * paragraph '0002! - paragraph '0003! *	1-10	

EPO FORM 1503 02.82 (P04C10)

**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 01 30 5020

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

20-07-2004

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
EP 1052718	A	15-11-2000	CA 2319460 A1	08-06-2000
			EP 1052718 A1	15-11-2000
			US 6365300 B1	02-04-2002
			WO 0033409 A1	08-06-2000
			JP 2000340257 A	08-12-2000
US 5314765	A	24-05-1994	NONE	
JP 2000340257	A	08-12-2000	CA 2319460 A1	08-06-2000
			EP 1052718 A1	15-11-2000
			WO 0033409 A1	08-06-2000
			US 6365300 B1	02-04-2002
JP 06310125	A	04-11-1994	NONE	
EP 0469574	A	05-02-1992	JP 4095351 A	27-03-1992
			JP 3184517 B2	09-07-2001
			JP 4202024 A	22-07-1992
			DE 69105658 D1	19-01-1995
			DE 69105658 T2	20-04-1995
			EP 0469574 A1	05-02-1992
			US 5217826 A	08-06-1993
US 5085953	A	04-02-1992	FR 2666803 A1	20-03-1992
			JP 4231346 A	20-08-1992
			US 5141614 A	25-08-1992
			US 5227148 A	13-07-1993

EPO FORM P0459

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

THIS PAGE BLANK (USPTO)